

Characterization of Leaks from Compressed Hydrogen Systems and Related Components

DOT-T-05-01

January, 2005



U.S. Department of Transportation
Research and Special Programs Administration

Office of Innovation Research and Education
400 7th St. SW
Washington, DC 20590

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE January 2005		3. REPORT TYPE AND DATES COVERED Final Report – January 2005
4. TITLE AND SUBTITLE Characterization of Leaks From Compressed Hydrogen Systems and Related Components			5. FUNDING NUMBERS	
6. AUTHOR(S) William P. Chernicoff,* Lisa Engblom* . William Houf **, Robert Schefer**, and Christopher San Marchi**				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) *RSPA – Office of Innovation Research and Education **Sandia National Laboratories Washington, DC 20590 Livermore, CA 94551			8. PERFORMING ORGANIZATION REPORT NUMBER DOT-T-05-01	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Department of Transportation Research and Special Programs Administration Office of Innovation Research and Education			10. SPONSORING/MONITORING AGENCY REPORT NUMBER DOT-T-05-01	
11. SUPPLEMENTARY NOTES none				
12a. DISTRIBUTION/AVAILABILITY STATEMENT This document is available to the public through the National Technical Information Service, Springfield, VA 22161			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The equations are developed for the calculation of leak flow rates in various leak regimes. Leaks due to pressure-driven convection and due to permeation through metals are considered. For convective leaks, the conditions under which the flow transitions from laminar to turbulent and from subsonic to choked (sonic) flow are discussed. Equations are presented to calculate leak rates for subsonic laminar and turbulent flows, as well as choked (sonic) flow rates. Given the advantages of using noncombustible gases for leak testing and measurement, equations are also developed for calculating the equivalent leak rate of helium when it is used as a surrogate for the combustible gases hydrogen and methane in each of these flow regimes. Equations are derived for the permeation rate of hydrogen through several common metals. Tabulated data is presented for the permeation rates of hydrogen through pure iron and two types of stainless steel over a pressure range from 5,000 psi to 15,000 psi and a temperature range of -40°C to 100°C. The results clearly show the sensitivity of flux to temperature, with over an order of magnitude increase in flux as the temperature is increased from ambient to 373 K (100°C). Permeation rates are also found to vary significantly with material. For example, permeation rates for pure iron (Fe) are about three orders of magnitude higher than 403 stainless steel and nearly five orders of magnitude higher than type 316L stainless steel for a given temperature and pressure. Under many combinations of pressure and temperature, leak rates for Fe exceed the permissible gaseous hydrogen leak rates, while rates for 316L stainless steel are well below permissible permeation rates at all combinations of temperature and pressure considered.				
14. SUBJECT TERMS hydrogen, hydrogen safety, leakage, permeation, fuel system design, system safety, alternative fuel			15. NUMBER OF PAGES 22	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	

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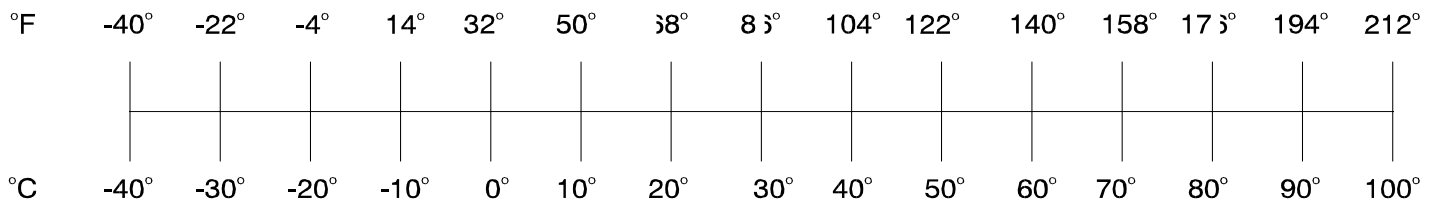
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English to Metric

LENGTH (Approximate) 1 inch (in) = 2.5 centimeters (cm) 1 foot (ft) = 30 centimeters (cm) 1 yard (yd) = 0.9 meter (m) 1 mile (mi) = 1.6 kilometers (km)	LENGTH (Approximate) 1 millimeter (mm) = 0.04 inch (in) 1 centimeter (cm) = 0.4 inch (in) 1 meter (m) = 3.3 feet (ft) 1 meter (m) = 1.1 yards (yd) 1 kilometer (km) = 0.6 mile (mi)
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TEMPERATURE (Exact) $[(x - 32)(5/9)]^{\circ}\text{F} = y^{\circ}\text{C}$ $(x + 460) / 1.8 = y^{\circ}\text{K}$	TEMPERATURE (Exact) $[(9/5)y + 32]^{\circ}\text{C} = x^{\circ}\text{F}$ $(y \times 1.8 - 460) = x^{\circ}\text{F}$
PRESSURE (Exact) 1 psi = 6.8948 k Pa	PRESSURE (Exact) 1 M Pa = 145.04 psi
ENERGY & ENERGY DENSITY (Exact) 1 Btu = 1.05506 kJ 1 Btu/lb = 2.326 kJ/kg	ENERGY & ENERGY DENSITY (Exact) 1 MJ = 947.81 Btu 1 MJ/kg = 430 Btu/lb

QUICK FAHRENHEIT-CELSIUS TEMPERATURE CONVERSION



CHARACTERIZATION OF LEAKS FROM COMPRESSED HYDROGEN SYSTEMS AND RELATED COMPONENTS

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Abstract

The equations are developed for the calculation of leak flow rates in various leak regimes. Leaks due to pressure-driven convection and due to permeation through metals are considered. For convective leaks, the conditions under which the flow transitions from laminar to turbulent and from subsonic to choked (sonic) flow are discussed. Equations are presented to calculate leak rates for subsonic laminar and turbulent flows, as well as choked (sonic) flow rates. Given the advantages of using noncombustible gases for leak testing and measurement, equations are also developed for calculating the equivalent leak rate of helium when it is used as a surrogate for the combustible gases hydrogen and methane in each of these flow regimes. Equations are derived for the permeation rate of hydrogen through several common metals. Tabulated data is presented for the permeation rates of hydrogen through pure iron and two types of stainless steel over a pressure range from 5,000 psi to 15,000 psi and a temperature range of -40°C to 100°C . The results clearly show the sensitivity of flux to temperature, with over an order of magnitude increase in flux as the temperature is increased from ambient to 373 K (100°C). Permeation rates are also found to vary significantly with material. For example, permeation rates for pure iron (Fe) are about three orders of magnitude higher than 403 stainless steel and nearly five orders of magnitude higher than type 316L stainless steel for a given temperature and pressure. Under many combinations of pressure and temperature, leak rates for Fe exceed the permissible gaseous hydrogen leak rates, while rates for 316L stainless steel are well below permissible permeation rates at all combinations of temperature and pressure considered.

Introduction

The system components expected to evolve during the future development of a hydrogen infrastructure include storage, bulk transportation and distribution, production and utilization. One common requirement that must be met in each of these components is the safe confinement and utilization of hydrogen. The identification of critical safety issues

thus becomes integral to hydrogen infrastructure development. To this end a recent workshop was held to identify safety scenarios and prioritize research and technical activities to support the development of hydrogen safety standards [1]. As part of this workshop, unintended releases of hydrogen were recognized as a critical safety issue that needs to be addressed. Of the sixty-eight release scenarios identified, the majority were leaks that resulted in combustible cloud formation. The leak size, its origin and surroundings were all used to further categorize the scenarios and resulting hazards.

It is generally recognized that two categories of leaks could be important in future hydrogen infrastructure components. The first of these is the leakage of gaseous hydrogen through holes, breaks and defects in material surfaces that contain the hydrogen. These leaks involve the convection of hydrogen through openings of various size and are driven by a pressure difference. They fall in the continuum flow regime, as opposed to the molecular flow regime, and involve openings that are many times the molecular mean free path. Gaseous convective leaks can further be divided into leaks from high-pressure sources and those from low-pressure sources, since the pressure ratio across the leak determines whether the flow through the leak is subsonic, or choked (sonic). For example, in the simple case of air passing through a small nozzle, if the pressure ratio across the nozzle is greater than about 1.9:1 the flow will be choked at the nozzle exit and the flow rate through the nozzle will be limited. In this case the flow is considered compressible and the equation set governing compressible flow behavior can be applied. At pressure ratios across the leak that are below the choked flow minimum, the flow is subsonic and governed by incompressible flow equations. Depending on leak geometry and flow rate, this subsonic flow can be either laminar or turbulent.

A second leak category is diffusion, or permeation, of hydrogen through the surface of the hydrogen confinement vessel. In this case the leak falls into the molecular flow regime and involves the diffusive transport of molecules through the surface material. This type of leak is probably most relevant to storage tanks that have a high surface area and long residence times where the leak occurs over an extended period of time. Again, this type of leak is governed by a different set of mathematical models.

Hydrogen system components will require periodic testing as to their integrity against leaks of various types. From the standpoint of both safety and cost, it is desirable to test for leaks and assess whether the leak rate is below a desired minimum standard from various components using an inert surrogate gas. Helium has been proposed as a good candidate for this procedure due to its low molecular weight and molecule size, which are comparable to, but not exactly matching, those of hydrogen.

The objective of this paper is twofold. The first objective is to provide a framework for the calculation of flow rates in various leak regimes. As such, the paper addresses both convectively driven gaseous hydrogen leaks and the permeation of hydrogen through metals. In the case of convective leaks, equations will be presented for determining leak rates for low-pressure (laminar and turbulent incompressible flow) and high-pressure (choked flow) leaks. Given the desirability of using an inert gas such as helium as a surrogate for combustible gas during leak testing, a second objective is to develop the

equations for calculating the equivalent flow rate of helium when it is used in leak testing as a surrogate for two common combustible gases, hydrogen and methane. In the following sections convective leaks are first considered, followed by a discussion of hydrogen permeation through metals. Convective leaks are further categorized into subsonic laminar and turbulent flows, and choked flows from high-pressure sources. In each case the governing equations are developed and used to determine the equivalent flow rates of a helium surrogate gas that replaces the hydrogen and methane.

Hydrogen Leakage

Gas leakage from gas storage and delivery systems typically occurs through an aperture that is much greater than the mean free path of the gas molecules. Therefore, a flow-based continuum model can be used to approximate the leakage rate. The highest pressures encountered typically range from 3,600 to 10,000 psi in storage tanks and 7,500 to 15,000 psi in the fueling system lines. However, downstream in a vehicle fuel system the actual pressure can be as low as 10 to 15 psig.

Swain and Swain [2] studied the leakage rates of both hydrogen and methane at line pressures up to about 14psi. They determined that leaks at low pressures occur primarily in a laminar mode, although entrance effects must be accounted for in leaks with large cross-sections [2]. Leaks at higher pressures occur in a turbulent regime, and leaks at very high pressures can be sonic [3]. The maximum allowable leak flow rates specified in NGV2 [4] and HGV2 [5] for natural gas and hydrogen, respectively, are given in the first column of Table 1. Shown in the remaining columns of Table 1 are the calculated equivalent helium leak rates for methane and hydrogen in different flow regimes based on the procedures described below.

Determination of Flow Regime

At lower pressures the flow can be treated as incompressible and can be either laminar or turbulent. The transition from laminar to turbulent flow should occur at approximately

the same Reynolds numbers $\left(Re = \frac{VD\rho}{\mu} \right)$ for all gases where V is the gas velocity, D is

an effective leak diameter, ρ is the gas density and μ is the dynamic viscosity [3]. For example, the transition Reynolds number for flow through a pipe is about 2,300. This value compares with flow studies in small diameter hydrogen and methane leaks that showed laminar behavior up to a Reynolds number of 3,200 [2]. Assuming the same physical defect causing the leak and the same pressure and velocity, it is the density to

viscosity ratio $\left(\frac{\rho}{\mu} \right)$, or the inverse of the kinematic viscosity (ν), that determines the

Reynolds number [3]. The kinematic viscosities of helium, hydrogen, and methane at 20°C are approximately $1.2 \cdot 10^{-4}$, $1.1 \cdot 10^{-4}$, and $1.3 \cdot 10^{-5}$ m²/s, respectively [6], so the density to viscosity ratios of methane to helium and hydrogen to helium are 9.3 and 1.1, respectively. Thus helium should begin to transition from laminar to turbulent flow at a

flow rate about 9.3 times greater than the flow rate where methane transitions and at a flow rate about 1.1 times greater than the flow rate where hydrogen transitions.

As the pressure ratio across the leak increases a transition from incompressible to compressible flow occurs and, at a sufficiently high-pressure ratio, the flow through the leak becomes sonic, or choked, at the leak exit. This limits the leak rate to a value that depends on the stagnation temperature and pressure of the gas, the leak diameter and the type of gas. Assuming isentropic flow of an ideal gas through a converging nozzle, the transition to sonic flow is determined by the pressure ratio across the leak, P_o/P_e , where P_o is the stagnation pressure of the gas on the high pressure side of the leak and P_e is the pressure at the leak exit. This ratio must exceed a value of 1.89 for sonic flow to occur in air. Since this pressure ratio is dependent on the ratio of specific heats at constant pressure and volume, k , it is of interest to examine how this ratio varies with the gas being considered. It can be shown that the pressure ratio across a converging nozzle under isentropic flow conditions required for choked flow at the minimum diameter is given by

$$\frac{P_o}{P_e} = \left[1 + \left(\frac{k-1}{2} \right) \right]^{\frac{k}{k-1}} \quad \text{Eq. (1)}$$

The specific heat ratios of helium, hydrogen, and methane at 20°C are 1.66, 1.41, and 1.31, respectively [8]. Substituting these values into Eq. (1) gives the critical pressure ratio for the transition to sonic flow for helium and hydrogen and methane to be 2.05, 1.90 and 1.84, respectively. Thus, for these three gases the variation in critical pressure ratio is less than 10 percent.

Laminar Flow Regime

Hagen-Poiseuille flow, which assumes laminar, pressure driven flow through a tube, can be used to describe leakage through a pinhole. The resulting volumetric flow rate through the leak, can then be determined by applying Darcy's equation to the flow:

$$Q = \frac{\Delta P \pi D^4}{128 \mu L} \quad \text{Eq. (2)}$$

where D is the leak diameter, μ is the dynamic viscosity of the gas, L is the length of the leak passageway, and ΔP is the pressure drop across the leak [2]. Helium is frequently used as the test gas to measure gas leakage. The maximum allowable leak rate for natural gas containers is specified in NGV2 as 0.25 cc per hour per liter of water capacity at 3,600 psi, or 0.25 cc/hr/liter at 3,600 psi [4]. Note that this allowable leak rate is specified as the volumetric leak rate at standard temperature and pressure (cc/hr) normalized by the volume from which the leak is flowing. The allowable leak rate from a given vessel is found by multiplying the normalized leak flow rate by the vessel volume. The ratio of the leak rate equation for helium and natural gas can be used to approximate

the equivalent leak rate for helium in terms of the allowable leak rate for natural gas (methane). Assuming flow in the same leak geometry and with the same pressure drop yields an equation of the form

$$Q_{He} = \frac{\mu_{CH_4}}{\mu_{He}} Q_{CH_4} \quad \text{Eq. (3)}$$

To illustrate the use of this equation, the equivalent leak rates for helium that correspond to the maximum permissible leak rates for methane and hydrogen in Table 1 will be determined. It is important to note that the permissible leak rates in Table 1 are for methane at 3,600 psi and hydrogen at 5,000 psi and 10,000 psi. Since leaks from such a high pressure source (for example a storage tank) typically exhaust into a surrounding environment at near atmospheric conditions, the resulting pressure ratio across the leak will exceed the critical pressure ratio for sonic flow and result in a sonic, choked flow and not a subsonic laminar or turbulent flow. The leak rates in the columns labeled laminar and turbulent are thus simply helium flow rate equivalencies to the permissible methane and hydrogen leak rates. The dynamic viscosities of helium and methane at 20°C are approximately 1.9×10^{-5} Ns/m² and 1.1×10^{-5} Ns/m², respectively [6]. Therefore, the equivalent helium leak rate is 0.14 cc/hr/liter.

The same process can be used to approximate the equivalent leak rates of helium in terms of allowable leak rates for hydrogen. The maximum allowable leak rate for hydrogen specified in HGV2 is 1 cc/hr/liter at 5,000 psi and 2.8 cc/hr/liter at 10,000 psi [5]. The dynamic viscosity of hydrogen at 20°C is about 8.5×10^{-6} Ns/m² [6]. The equivalent helium leak rates are 0.45 cc/hr/liter at 5,000 psi and 1.25 cc/hr/liter at 10,000 psi. These equivalent leak rate values are given in the third column of Table 1.

Turbulent Flow Regime

Darcy's equation with a constant friction factor can be used to approximate the leak rate for a turbulent regime. In general, the friction factor, f , for turbulent flows is a function of both surface roughness and Reynolds number [7]. However, for a fixed surface roughness, if it is assumed that the flow is fully turbulent then the friction factor can be taken as constant. Given these assumptions the volumetric flow rate for turbulent flow is given by:

$$Q = 0.354 \pi \frac{D^{2.5} \sqrt{\Delta P}}{\sqrt{f L \rho}} \quad \text{Eq. (4)}$$

where f is the Darcy friction factor and ρ is the gas density [2]. Again, for the same leak geometry, surface roughness and pressure drop across the leak, the equivalent leak rate between helium and methane or helium and hydrogen is found by taking the ratios of the leak rates,

$$Q_{He} = \frac{\sqrt{\rho_{CH_4}}}{\sqrt{\rho_{He}}} Q_{CH_4} \quad \text{or} \quad Q_{He} = \frac{\sqrt{\rho_{H_2}}}{\sqrt{\rho_{He}}} Q_{H_2} \quad \text{Eq. (5)}$$

Assuming that all of the gases behave as ideal gases allows Eq. (5) to be further simplified. While the assumption of an ideal gas is not valid at sufficiently high pressures, it should be a good approximation for the turbulent regime since the pressure drop across the leak will be less than a factor of two. Pressure drops greater than a factor of two typically result in sonic flow at the leak exit and the compressible flow regime described below is entered.

Assuming ideal gas behavior and, further, that the pressure and temperature of the three gases are the same, Eq. (5) can be simplified to

$$Q_{He} = \frac{\sqrt{M_{CH_4}}}{\sqrt{M_{He}}} Q_{CH_4} \quad \text{or} \quad Q_{He} = \frac{\sqrt{M_{H_2}}}{\sqrt{M_{He}}} Q_{H_2} \quad \text{Eq. (6)}$$

where M_i is the molecular weight of the i th specie. The molecular weights of hydrogen, helium, and methane are 2, 4, and 16 kg/kmol, respectively. The equivalent helium leakage rate for methane is 0.5 cc/hr/liter, and the rates for hydrogen at 5,000 and 10,000 psi are 0.71 and 1.98 cc/hr/liter, respectively. These leak rates are given in the fourth column of Table 1.

Sonic Throttling Flow

At sufficiently high pressure ratios the flow through a leak becomes sonic, or choked, at the leak exit. If it is assumed that the flow through the leak can be modeled as an isentropic flow of an ideal gas through a converging nozzle, then well-established relationships for compressible flow can be applied to determine flow-equivalency relations for different gases. As described previously, choked flow requires that the pressure ratio across the leak, P_o/P_e , exceeds a critical value (1.9 for hydrogen) where P_o is the stagnation pressure in, for example, a gas storage tank and P_e is the pressure at the leak exit. Under these conditions it can be shown that the volumetric flow rate (at standard temperature and pressure) of an ideal gas through the leak is given by,

$$Q = \frac{A_c}{\rho_{stp}} \left[k P_o \rho_o \left(\frac{2}{k+1} \right)^{\frac{k+1}{k-1}} \right]^{\frac{1}{2}} \quad \text{Eq. (7)}$$

where A_c is the critical area of the leak passage at its minimum diameter, k is the ratio of specific heats at constant pressure and volume, P_0 and ρ_0 are the stagnation pressure and density of the gas, respectively, and ρ_{stp} is the gas density at standard temperature and pressure. Taking the ratio of the leak rates and assuming identical leak geometry with identical stagnation temperature and pressure, the equivalent leak rate (for ideal gases) can be calculated as

$$Q_{He} = \left(\frac{M_{CH_4}}{M_{He}} \right)^{\frac{1}{2}} \frac{g(k_{He})}{g(k_{CH_4})} Q_{CH_4} \quad \text{or} \quad Q_{He} = \left(\frac{M_{H_2}}{M_{He}} \right)^{\frac{1}{2}} \frac{g(k_{He})}{g(k_{H_2})} Q_{H_2} \quad \text{Eq. (8)}$$

where the function $g(k)$ has been defined for the i th specie

$$g(k_i) = \left[k_i \left(\frac{2}{k_i + 1} \right)^{\frac{k_i + 1}{k_i - 1}} \right]^{\frac{1}{2}}. \quad \text{Eq. (9)}$$

While the ideal gas assumption is valid for the lower pressure ranges encountered in both the laminar and turbulent flow regimes, it is important to note that the ideal gas approximation may not be a good model for hydrogen at high pressures. At approximately 10,000 psi and 300K the compressibility factor Z (where $Z=P/(\rho RT)$) is about 1.5 for hydrogen. For an ideal gas, Z is equal to unity. It is also noted that the assumption of isentropic expansion neglects the effect of friction along the walls of the leak passageway which, depending on the leak geometry and passageway length, may be significant and, in some cases, can also result in choked flow. The specific heat ratios of helium, hydrogen, and methane at 20°C are 1.66, 1.41, and 1.31, respectively [8]. Thus, the equivalent helium leakage rate for methane is 0.54 cc/hr/liter, and the rates for hydrogen at 5000 and 10,000 psi are 0.75 and 2.09 cc/hr/liter, respectively. These equivalent leak rates are given in the last column of Table 1.

	Permissible* Flow Rate	Laminar Flow	Turbulent Flow	Sonic Flow**
Methane at 3,600psi	0.25	0.14	0.5	0.54
Hydrogen at 5,000psi	1	0.45	0.71	0.75
Hydrogen at 10,000psi	2.8	1.25	1.98	2.09

Table 1. Helium Equivalent Leak Rate in cc/hr/liter. *Permissible methane and hydrogen flow rates from references [4, 5]. **Equivalent flow sonic flow rates based on Eq.(8).

While the ideal gas assumption yields a much simplified and therefore useful equation for equivalent leak rates between different gases, as noted above the ideal gas approximation may not be a good model for gases at high pressures. Departures from ideal gas behavior can be approximately included in the analysis by allowing for a non-unity compressibility

factor, Z . Using a non-deal gas equation of state ($P=Z\rho RT$) and sound speed leads to the following equivalent leak rate equations for sonic flow of non-ideal gases

$$Q_{He} = \left(\frac{M_{CH_4}}{M_{He}} \right)^{\frac{1}{2}} \left(\frac{Z_{CH_4}}{Z_{He}} \right)^{\frac{1}{2}} \frac{g(k_{He})}{g(k_{CH_4})} Q_{CH_4} \quad \text{or} \quad Q_{He} = \left(\frac{M_{H_2}}{M_{He}} \right)^{\frac{1}{2}} \left(\frac{Z_{H_2}}{Z_{He}} \right)^{\frac{1}{2}} \frac{g(k_{He})}{g(k_{H_2})} Q_{H_2} \quad \text{Eq. (10)}$$

The compressibility factor, Z , is a function of pressure and temperature for a given gas. As a first approximation the compressibility factor can be evaluated at the tank stagnation pressure and temperature (P_o , T_o). Values of the compressibility factor for methane, helium, and hydrogen at various pressures and temperatures can be found in references [9], [10], and [11] respectively.

Helium-Nitrogen Mixtures

If a mixture of helium-nitrogen is used, the same basic equations will apply using properties of the mixture. The helium volumetric leak rate is then computed from the mixture volumetric leak rate by using the expression $Q_{He} = x_{He} Q_{mix}$, where x_{He} is the mole, or volume fraction of helium in the helium-nitrogen mixture. The modified equations for laminar and turbulent flows are shown below.

Laminar Flow

$$Q_{He} = \frac{\mu_{CH_4} \Delta P_{mix}}{\mu_{mix} \Delta P_{CH_4}} Q_{CH_4} \quad \text{or} \quad Q_{He} = \frac{\mu_{H_2} \Delta P_{mix}}{\mu_{mix} \Delta P_{H_2}} Q_{H_2} \quad \text{Eq. (11)}$$

Turbulent Flow

$$Q_{He} = \frac{\sqrt{M_{CH_4}}}{\sqrt{M_{mix}}} \frac{\sqrt{\Delta P_{mix}}}{\sqrt{\Delta P_{CH_4}}} Q_{CH_4} \quad \text{or} \quad Q_{He} = \frac{\sqrt{M_{H_2}}}{\sqrt{M_{mix}}} \frac{\sqrt{\Delta P_{mix}}}{\sqrt{\Delta P_{H_2}}} Q_{H_2} \quad \text{Eq. (12)}$$

These equations can be further simplified by assuming ideal gas behavior and the same total pressure drop for the different gases ($\Delta P_{Total} = \Delta P_{H_2} = \Delta P_{CH_4} = \Delta P_{mix}$). Equations (11) and (12) take the form

Laminar Flow

$$Q_{He} = \frac{\mu_{CH_4}}{\mu_{mix}} x_{He} Q_{CH_4} \quad \text{or} \quad Q_{He} = \frac{\mu_{H_2}}{\mu_{mix}} x_{He} Q_{H_2} \quad \text{Eq. (13)}$$

Turbulent Flow

$$Q_{He} = \frac{\sqrt{M_{CH_4}}}{\sqrt{M_{mix}}} x_{He} Q_{CH_4} \quad \text{or} \quad Q_{He} = \frac{\sqrt{M_{H_2}}}{\sqrt{M_{mix}}} x_{He} Q_{H_2} \quad \text{Eq. (14)}$$

The mixture molecular weight and mixture viscosity can be calculated from expressions of the form

$$M_{mix} = \sum_i x_i M_i, \quad \mu_{mix} = \sum_i x_i \mu_i \quad \text{Eq. (15)}$$

where x_i is the mole fraction of species i , and M_i and μ_i are the molecular weight and viscosity of species i , respectively.

In the case of sonic flow Eqs. 8 and 10 still apply, but the effect of nitrogen mixed with helium will have to be accounted for through its effect on the mixture molecular weight, M_{mix} and specific heat ratio, k_{mix} , which will have to be used in place of M_{He} and k_{He} . In the case of Eq. 10 the compressibility, Z_{He} for helium must be replaced by the compressibility of the mixture Z_{mix} . The values of M_{mix} can be calculated from the expression above. The value of k_{mix} and Z_{mix} can be calculated from the equations

$$C_{p_{mix}} = \sum_i x_i C_{p_i}, \quad C_{v_{mix}} = \sum_i x_i C_{v_i}, \quad Z_{mix} = \sum_i x_i Z_i \quad \text{Eq. (16)}$$

where C_{p_i} and C_{v_i} are the constant pressure specific heat and constant volume specific heat of species i , and Z_i is the compressibility of species i , respectively. Then, by definition

$$k_{mix} = \frac{C_{p_{mix}}}{C_{v_{mix}}} \quad \text{Eq. (17)}$$

Equations 8 and 10 are used to calculate the mixture volumetric flow rate of the leak. The expression ($Q_{He} = x_{He} Q_{mix}$) is then used to compute the helium volumetric flow rate from the mixture volumetric flow rate.

Table 2 shows the helium equivalent leak rates for a helium-nitrogen mixture with 10% helium.

	Permissible Flow Rate*	Laminar Flow	Turbulent Flow	Sonic Flow
Methane at 3,600psi	0.25	0.016	0.020	0.0206
Hydrogen at 5,000psi	1	0.050	0.028	0.0285
Hydrogen at 10,000psi	2.8	0.139	0.078	0.0798

Table 2 - Helium Equivalent Leak Rate in cc/hr/liter for 10% He mixture. *Permissible methane and hydrogen flow rates from references [4, 5].

Permeability in Metals

Permeation through the material wall takes place on a much smaller scale than leakage and must be modeled as diffusion through a solid rather than flow. In general, the permeation of hydrogen through a metal is quite complex and involves the adsorption and dissociation of molecular hydrogen to atomic hydrogen on the first surface. This process is followed by the diffusion of atomic hydrogen through the metal to the second surface where they recombine and undergo desorption. Since hydrogen and helium diffuse through different mechanisms and the helium diffusion rate is several orders of magnitude slower, leak tests involving permeation through metals must be done with hydrogen. An approximation for the permeation rate of hydrogen through the walls of a metal tank can be found as follows. Consider an infinite plate of thickness l with high partial pressure of hydrogen on one side P and a comparatively negligible pressure on the other side of the plate. Fick's first law for diffusion provides the relationship between the hydrogen flux J and the concentration gradient across the plate. Sievert's law states that the concentration C is proportional to the square root of the pressure. Combining these relationships at steady state provides an expression for the rate of permeation of hydrogen by diffusion:

$$J = D \frac{\Delta C}{l} = \frac{DS\sqrt{P}}{l} \quad \text{Eq. (18)}$$

where J is the permeation rate [$\text{mol s}^{-1} \text{m}^{-2}$], D is the diffusivity of hydrogen in the plate material, and S is the solubility of hydrogen in the plate material [12]. The product of the solubility and the diffusivity is the permeability and has the expected exponential dependence on temperature:

$$\Phi = DS = \Phi_o \exp(-E_\Phi / RT) \quad \text{Eq. (19)}$$

The units of permeability are typically expressed in [$\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-1}\cdot\text{MPa}^{-1/2}$]. Hydrogen permeability data are provided in Table 3 for several metals. It should also be noted that there is significant scatter in data reported in the literature, perhaps in part due to the fact that permeability data are often extrapolated from high temperature and low pressure (these data, including much of the data reported here, are typically determined at temperatures $> 373 \text{ K}$ (100°C) and pressures $\leq 0.1 \text{ MPa}$). The data in Table 3 are provided as examples and no attempt was made to review or analyze data from the literature.

At high pressures and low temperatures, hydrogen does not behave as an ideal gas and the fugacity f should be used in place of the pressure in Eq. (18) to account for nonideality. The fugacity essentially describes the nonideal behavior of the gas and, in principle, can be determined from the equation of state. Many forms of the equation of state of hydrogen have been proposed, but in general these do not lend themselves to simple analytical forms for the fugacity as a function of pressure and temperature. For the purposes of permeability, we use the Abel-Noble form of the equation of state for its

simplicity and analytical tractability. The fugacity is derived from the Abel-Noble equation of state and has the form:

$$f = P \exp(Pb/RT) \quad \text{Eq. (20)}$$

where the “co-volume” constant $b = 15.5 \text{ cm}^3/\text{mole}$ [18]. This single constant describes the nonideal behavior of deuterium in the temperature range 200 to 350 K and pressures up to about 160 MPa. Although the constant b is derived for deuterium, Ref. [19] shows that hydrogen and deuterium behave nominally the same near ambient temperature and pressures up to 200 MPa.

Thus, the diffusion flux of hydrogen through a solid plate at steady state can then be expressed as

$$J = \frac{\Phi \sqrt{f}}{l} \quad \text{Eq. (21)}$$

This analysis assumes diffusion-limited conditions (i.e. surface absorption and desorption are not rate limiting).

Figure 1 shows the permeation flux of hydrogen as a function of pressure at two temperatures; results are shown for pure iron (Fe) and several types of stainless steel. Data from Table 3 is used to construct this plot and the thickness of the plate is assumed to be 5 mm. Pressure vessel and piping steels are expected to have a permeability near that of pure iron (due to low alloying content and similar crystal structure, compare the permeability of 4130 steel to iron in Table 3). The results show that differences of several orders of magnitude exist in the permeation rates through the different metals considered. The highest permeation rates are found for pure iron, while 316 stainless steel has a hydrogen flux nearly 5 orders of magnitude lower for the same pressure. The results presented in Fig. 1 for temperatures of 298 K and 373 K also clearly show the sensitivity of flux to temperature, with over an order of magnitude increase in flux with an increase in temperature from ambient to 373 K (100°C). Table 4 provides the permeability of several ferrous materials as a function of temperature in the range from 233 K (-40°C) to 373 K (100°C).

It is also of interest to determine permeation rates under the conditions and scenarios expected in the currently developing hydrogen infrastructure. For example, typical wall thickness for hydrogen storage tanks, transport vessels and delivery lines might vary from 0.5 mm to greater than 25 mm. Hydrogen tanks and tubing are certified for use between 233K (-40°C) and 358 K (85°C) and are expected for pressures up to 103 MPa (15000 psi). Tables 5 through 13 show the calculated variation in the permeation rate of hydrogen for this range of conditions using pure iron, and type 403 and 316 stainless steel as the wall material. The mass flux of hydrogen, J_v , in the third column is found by multiplying the molar flow rate from Eq. (21) by the molecular weight of hydrogen (2.016 gm/mole). The corresponding volumetric flow rates at STP, Q_v , are shown in the fourth column of each table.

Material	$\Phi = DS = \Phi_o \exp(-E_\Phi / RT)$		$\Phi_{\text{at 298K}}$ [mol·s ⁻¹ ·m ⁻¹ ·MPa ^{-1/2}]	Ref.
	Φ_o [mol·s ⁻¹ ·m ⁻¹ ·MPa ^{-1/2}]	E_Φ [kJ/mol]		
Pure Fe	5.35 x 10 ⁻⁵	33.6	6.9 x 10 ⁻¹¹	[13]
403 stainless steel	5.9 x 10 ⁻⁵	42.7	1.9 x 10 ⁻¹²	[14]
316L stainless steel	3.9 x 10 ⁻⁴	64.1	2.3 x 10 ⁻¹⁵	[12]
4130 steel	---	---	~10 ⁻¹¹	[15]
Aluminum	1.0 x 10 ⁻⁶	52.5	6.3 x 10 ⁻¹⁶	[16]
Copper	8.4 x 10 ⁻⁴	77.4	2.3 x 10 ⁻¹⁷	[17]
Gold†	1.14 x 10 ⁻³	115	7.9 x 10 ⁻²⁴	[17]

Table 3. Hydrogen permeability data from the literature [mol H₂·s⁻¹·m⁻¹·MPa^{-1/2}]. † data for deuterium permeation

Temperature (°C)	Φ [mol·s ⁻¹ ·m ⁻¹ ·MPa ^{-1/2}]		
	pure Fe	403 SS	316L SS
-40	1.57E-12	1.58E-14	1.70E-18
0	1.99E-11	3.99E-13	2.16E-16
10	3.36E-11	7.75E-13	5.85E-16
25	6.90E-11	1.93E-12	2.30E-15
50	1.97E-10	7.34E-12	1.70E-14
85	6.70E-10	3.47E-11	1.76E-13
100	1.05E-09	6.18E-11	4.17E-13

Table 4. Hydrogen permeability as a function of temperature for several ferrous materials and data from Table 3.

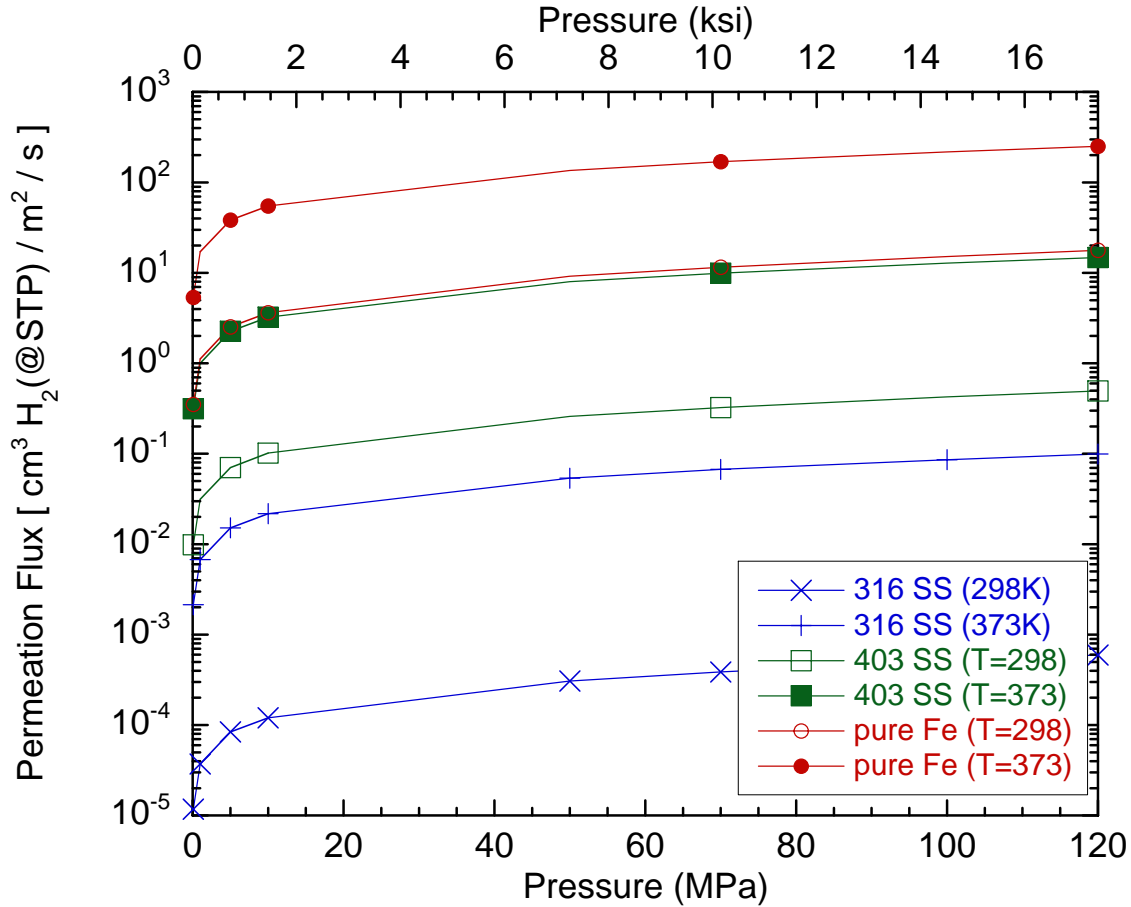


Figure 1. Permeation flux of hydrogen gas as a function of pressure through a 5 mm thick plate assuming permeability data from Table 3.

Finally, to compare the magnitude of the wall permeation rates with the permissible gas leak rates of Table 1, we assume a square box of one-liter volume. Since the permissible leak rates of Table 1 are in units of cc/hr/liter of stored gas, the values in Table 1 are just equal to the leak rate from the one-liter box. Using the surface area of this box, the permeation rates in Tables 5-13 can be converted to total volumetric flow rates at STP, Q_{H_2} . These are shown in the fifth column of the tables. (Note that for other container shapes the permeation rates in column 5 of these tables will have to be modified to account for difference in surface-to-volume ratio.) Depending on the conditions, it is seen that the volumetric flow rates in Tables 5 through 13 often exceed the permissible flow rates from HGV2 [5] for hydrogen at 34.4 and 68.9 MPa (5,000 and 10,000 psi), as seen in Table 1. In several cases they are two orders of magnitude higher. Even at 34.4 MPa (5000 psi), permeation rates through a wall using pure iron with a wall thickness of 0.5 mm exceed the permissible rate except at the lowest temperatures. At the highest pressure calculated (34.4 MPa / 15000 psi), the permeation rates are dangerously high for a wall thickness of 0.5 mm; it should be noted that a combination of wall thickness and pressure of 0.5 mm and 103 MPa is a hypothetical case since the stress in the wall of such a component would be too high for any practical engineering system. For the 403 stainless steel, permeation rates are generally permissible except at temperatures well above

ambient (greater than 323K / 50°C). For a wall thickness greater than 6.35 mm (0.25 in), permeation is maintained below the permissible rate for all conditions calculated except the highest temperatures and pressures with pure iron. The 316 stainless steel maintains permeation rates below the permissible value for all conditions studied.

P = 34.4 MPa (5000 psi)	L = 0.5 mm (0.02 in)			
Material	T (°C)	J_v (kg/m²s)	Q_v (cm³/s cm²)	Q_{H2} (cm³/hr)
Pure Fe	-40	4.3E-11	4.7E-08	0.10
	0	5.3E-10	5.9E-07	1.3
	10	8.9E-10	9.9E-07	2.1
	25	1.8E-09	2.0E-06	4.4
	50	5.2E-09	5.7E-06	12
	85	1.7E-08	1.9E-05	42
	100	2.7E-08	3.0E-05	65
403 Stainless	-40	4.3E-13	4.8E-10	1.0E-03
	0	1.1E-11	1.2E-08	0.026
	10	2.1E-11	2.3E-08	0.049
	25	5.1E-11	5.7E-08	0.12
	50	1.9E-10	2.1E-07	0.46
	85	9.0E-10	1.0E-06	2.2
	100	1.6E-09	1.8E-06	3.8
316 Stainless	-40	4.6E-17	5.1E-14	1.1E-07
	0	5.7E-15	6.4E-12	1.4E-05
	10	1.6E-14	1.7E-11	3.7E-05
	25	6.1E-14	6.8E-11	1.5E-04
	50	4.5E-13	5.0E-10	1.1E-03
	85	4.5E-12	5.1E-09	1.1E-02
	100	1.1E-11	1.2E-08	0.026

Table 5. Hydrogen permeation rates through metals.

P = 34.4 MPa (5000 psi)	L = 2.54 mm (0.10 in)			
Material	T (°C)	J_v (kg/m²s)	Q_v (cm³/s cm²)	Q_{H2} (cm³/hr)
Pure Fe	-40	8.4E-12	9.3E-09	0.020
	0	1.0E-10	1.2E-07	0.25
	10	1.8E-10	2.0E-07	0.42
	25	3.6E-10	4.0E-07	0.86
	50	1.0E-09	1.1E-06	2.4
	85	3.4E-09	3.8E-06	8.2
	100	5.4E-09	6.0E-06	13

403 Stainless	-40	8.4E-14	9.4E-11	2.0E-04
	0	2.1E-12	2.3E-09	5.0E-03
	10	4.0E-12	4.5E-09	9.7E-03
	25	1.0E-11	1.1E-08	0.024
	50	3.8E-11	4.2E-08	0.091
	85	1.8E-10	2.0E-07	0.43
	100	3.1E-10	3.5E-07	0.75
316 Stainless	-40	9.1E-18	1.0E-14	2.2E-08
	0	1.1E-15	1.3E-12	2.7E-06
	10	3.1E-15	3.4E-12	7.3E-06
	25	1.2E-14	1.3E-11	2.9E-05
	50	8.8E-14	9.8E-11	2.1E-04
	85	8.9E-13	9.9E-10	2.1E-03
	100	2.1E-12	2.4E-09	5.1E-03

Table 6. Hydrogen permeation rates through metals.

P = 34.4 MPa (5000 psi)	L = 6.35 mm (0.25 in)			
Material	T (°C)	J_v (kg/m²s)	Q_v (cm³/s cm²)	Q_{H2} (cm³/hr)
Pure Fe	-40	3.4E-12	3.7E-09	8.1E-03
	0	4.2E-11	4.6E-08	0.10
	10	7.0E-11	7.8E-08	0.17
	25	1.4E-10	1.6E-07	0.34
	50	4.1E-10	4.5E-07	0.97
	85	1.4E-09	1.5E-06	3.3
	100	2.1E-09	2.4E-06	5.1
403 Stainless	-40	3.4E-14	3.8E-11	8.1E-05
	0	8.4E-13	9.3E-10	2.0E-03
	10	1.6E-12	1.8E-09	3.9E-03
	25	4.0E-12	4.5E-09	9.6E-03
	50	1.5E-11	1.7E-08	0.036
	85	7.1E-11	7.9E-08	0.17
	100	1.3E-10	1.4E-07	0.30
316 Stainless	-40	3.6E-18	4.0E-15	8.7E-09
	0	4.5E-16	5.0E-13	1.1E-06
	10	1.2E-15	1.4E-12	2.9E-06
	25	4.8E-15	5.3E-12	1.1E-05
	50	3.5E-14	3.9E-11	8.4E-05
	85	3.6E-13	4.0E-10	8.6E-04

	100	8.5E-13	9.4E-10	2.0E-03
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Table 7. Hydrogen permeation rates through metals.

P = 51.7 MPa (7500 psi)	L = 0.5 mm (0.02 in)			
Material	T (°C)	J_v (kg/m²s)	Q_v (cm³/s cm²)	Q_{H2} (cm³/hr)
Pure Fe	-40	5.6E-11	6.2E-08	0.13
	0	6.9E-10	7.7E-07	1.7
	10	1.2E-09	1.3E-06	2.8
	25	2.4E-09	2.6E-06	5.6
	50	6.6E-09	7.4E-06	16
	85	2.2E-08	2.5E-05	53
	100	3.5E-08	3.9E-05	84
403 Stainless	-40	5.6E-13	6.3E-10	1.4E-03
	0	1.4E-11	1.5E-08	0.033
	10	2.7E-11	3.0E-08	0.064
	25	6.6E-11	7.3E-08	0.16
	50	2.5E-10	2.7E-07	0.59
	85	1.2E-09	1.3E-06	2.8
	100	2.0E-09	2.3E-06	4.9
316 Stainless	-40	6.1E-17	6.7E-14	1.5E-07
	0	7.5E-15	8.3E-12	1.8E-05
	10	2.0E-14	2.2E-11	4.8E-05
	25	7.9E-14	8.7E-11	1.9E-04
	50	5.7E-13	6.4E-10	1.4E-03
	85	5.8E-12	6.5E-09	0.014
	100	1.4E-11	1.5E-08	0.033

Table 8. Hydrogen permeation rates through metals.

P = 51.7 MPa (7500 psi)	L = 2.54 mm (0.1 in)			
Material	T (°C)	J_v (kg/m²s)	Q_v (cm³/s cm²)	Q_{H2} (cm³/hr)
Pure Fe	-40	1.1E-11	1.2E-08	0.026
	0	1.4E-10	1.5E-07	0.33
	10	2.3E-10	2.5E-07	0.55
	25	4.6E-10	5.1E-07	1.11
	50	1.3E-09	1.5E-06	3.1
	85	4.4E-09	4.9E-06	10.5
	100	6.8E-09	7.6E-06	16

403 Stainless	-40	1.1E-13	1.2E-10	2.7E-04
	0	2.7E-12	3.0E-09	6.5E-03
	10	5.2E-12	5.8E-09	0.013
	25	1.3E-11	1.4E-08	0.031
	50	4.9E-11	5.4E-08	0.12
	85	2.3E-10	2.5E-07	0.54
	100	4.0E-10	4.5E-07	0.96
316 Stainless	-40	1.2E-17	1.3E-14	2.9E-08
	0	1.5E-15	1.6E-12	3.5E-06
	10	4.0E-15	4.4E-12	9.5E-06
	25	1.5E-14	1.7E-11	3.7E-05
	50	1.1E-13	1.3E-10	2.7E-04
	85	1.1E-12	1.3E-09	2.8E-03
	100	2.7E-12	3.0E-09	6.5E-03

Table 9. Hydrogen permeation rates through metals.

P = 51.7 MPa (7500 psi)	L = 6.35 mm (0.25 in)			
Material	T (C)	J_v (kg/m²s)	Q_v (cm³/s cm²)	Q_{H2} (cm³/hr)
Pure Fe	-40	4.4E-12	4.9E-09	0.011
	0	5.4E-11	6.0E-08	0.13
	10	9.1E-11	1.0E-07	0.22
	25	1.9E-10	2.1E-07	0.44
	50	5.2E-10	5.8E-07	1.3
	85	1.7E-09	1.9E-06	4.2
	100	2.7E-09	3.0E-06	6.6
403 Stainless	-40	4.4E-14	4.9E-11	1.1E-04
	0	1.1E-12	1.2E-09	2.6E-03
	10	2.1E-12	2.3E-09	5.0E-03
	25	5.2E-12	5.8E-09	0.012
	50	1.9E-11	2.2E-08	0.047
	85	9.1E-11	1.0E-07	0.22
	100	1.6E-10	1.8E-07	0.39
316 Stainless	-40	4.8E-18	5.3E-15	1.1E-08
	0	5.9E-16	6.5E-13	1.4E-06
	10	1.6E-15	1.8E-12	3.8E-06
	25	6.2E-15	6.9E-12	1.5E-05
	50	4.5E-14	5.0E-11	1.1E-04
	85	4.6E-13	5.1E-10	1.1E-03
	100	1.1E-12	1.2E-09	2.6E-03

Table 10. Hydrogen permeation rates through metals.

P = 103 MPa (15000 psi)	L = 0.5 mm (0.02 in)			
Material	T (°C)	J_v (kg/m²s)	Q_v (cm³/s cm²)	Q_{H2} (cm³/hr)
Pure Fe	-40	9.7E-11	1.1E-07	0.23
	0	1.2E-09	1.3E-06	2.8
	10	1.9E-09	2.2E-06	4.7
	25	3.9E-09	4.3E-06	9.4
	50	1.1E-08	1.2E-05	26
	85	3.6E-08	4.0E-05	86
	100	5.6E-08	6.2E-05	134
403 Stainless	-40	9.8E-13	1.1E-09	2.4E-03
	0	2.3E-11	2.6E-08	0.056
	10	4.5E-11	5.0E-08	0.107
	25	1.1E-10	1.2E-07	0.26
	50	4.1E-10	4.5E-07	0.97
	85	1.9E-09	2.1E-06	4.5
	100	3.3E-09	3.6E-06	7.9
316 Stainless	-40	1.1E-16	1.2E-13	2.5E-07
	0	1.3E-14	1.4E-11	3.0E-05
	10	3.4E-14	3.8E-11	8.1E-05
	25	1.3E-13	1.5E-10	3.1E-04
	50	9.4E-13	1.0E-09	2.3E-03
	85	9.4E-12	1.0E-08	0.023
	100	2.2E-11	2.5E-08	0.053

Table 11. Hydrogen permeation rates through metals.

P = 103 MPa (15000 psi)	L = 2.54 mm (0.10 in)			
Material	T (°C)	J_v (kg/m²s)	Q_v (cm³/s cm²)	Q_{H2} (cm³/hr)
Pure Fe	-40	1.9E-11	2.1E-08	0.046
	0	2.3E-10	2.5E-07	0.55
	10	3.8E-10	4.2E-07	0.92
	25	7.7E-10	8.6E-07	1.8
	50	2.1E-09	2.4E-06	5.1
	85	7.1E-09	7.9E-06	17
	100	1.1E-08	1.2E-05	26
403 Stainless	-40	1.9E-13	2.1E-10	4.6E-04

	0	4.6E-12	5.1E-09	1.1E-02
	10	8.8E-12	9.8E-09	0.021
	25	2.2E-11	2.4E-08	0.052
	50	8.0E-11	8.9E-08	0.19
	85	3.7E-10	4.1E-07	0.88
	100	6.5E-10	7.2E-07	1.6
316 Stainless	-40	2.1E-17	2.3E-14	5.0E-08
	0	2.5E-15	2.8E-12	6.0E-06
	10	6.6E-15	7.4E-12	1.6E-05
	25	2.6E-14	2.9E-11	6.2E-05
	50	1.9E-13	2.1E-10	4.5E-04
	85	1.9E-12	2.1E-09	4.5E-03
	100	4.4E-12	4.8E-09	0.010

Table 12. Hydrogen permeation rates through metals.

P = 103 MPa (15000 psi)	L = 6.35 mm (0.25 in)			
Material	T (°C)	J_v (kg/m²s)	Q_v (cm³/s cm²)	Q_{H2} (cm³/hr)
Pure Fe	-40	7.7E-12	8.5E-09	0.018
	0	9.2E-11	1.0E-07	0.22
	10	1.5E-10	1.7E-07	0.37
	25	3.1E-10	3.4E-07	0.74
	50	8.6E-10	9.5E-07	2.1
	85	2.8E-09	3.1E-06	6.8
	100	4.4E-09	4.9E-06	10.6
403 Stainless	-40	7.7E-14	8.6E-11	1.9E-04
	0	1.8E-12	2.0E-09	4.4E-03
	10	3.5E-12	3.9E-09	8.5E-03
	25	8.6E-12	9.6E-09	0.021
	50	3.2E-11	3.5E-08	0.077
	85	1.5E-10	1.6E-07	0.35
	100	2.6E-10	2.9E-07	0.62
316 Stainless	-40	8.3E-18	9.2E-15	2.0E-08
	0	9.9E-16	1.1E-12	2.4E-06
	10	2.7E-15	3.0E-12	6.4E-06
	25	1.0E-14	1.1E-11	2.5E-05
	50	7.4E-14	8.2E-11	1.8E-04
	85	7.4E-13	8.2E-10	1.8E-03
	100	1.7E-12	1.9E-09	4.2E-03

Table 13. Hydrogen permeation rates through metals.

Summary

A framework is provided for the calculation of leak flow rates in various leak regimes. Leaks due to pressure-driven convection and due to permeation through metals are considered. The criteria used to define conditions under which the flow transitions between the various flow regimes are discussed. Equations are presented to calculate leak rates for subsonic laminar and turbulent flows as well as choked (sonic) flow rates. Given the advantages of using noncombustible gases for leak testing and measurement, equations are also developed for calculating the equivalent leak rate of helium when it is used as a surrogate for the combustible gases hydrogen and methane in each of these flow regimes.

Equations are also presented for the permeation rate of hydrogen through metals that show promise as materials for construction of hydrogen confinement vessels. Tabulated data is presented and compared for the permeation rates of hydrogen through pure iron and two types of stainless steel over a pressure range from 5,000 psi to 15,000 psi and a temperature range of -40°C to 100°C . The results show the sensitivity of flux to temperature, with over an order of magnitude increase in flux with an increase in temperature from ambient to 373 K (100°C). Hydrogen permeation rates are significantly higher for pure iron (Fe) than for either 403 or 316L stainless steel and, under many combinations of pressure and temperature, often exceed the maximum permissible leak rates for gaseous hydrogen. Depending on wall thickness, pressure and temperature, permeation rates with type 403 SS stainless steel are up to three orders of magnitude lower than for Fe and are typically below permissible leak rates. Permeation rates for type 316L nearly five orders of magnitude lower than Fe and, under all combinations of pressure and temperature, are always well below the permissible leak rates.

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